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Publication date:
2010

Document Version
Publisher's PDF, also known as Version of record

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Introduction

In the past years, there has been a rising demand for efficient heterogeneously catalyzed oxidation processes for production of both fine and bulk chemicals [1]. In order to avoid waste generation, considerable effort has been put into the development of aerobic oxidation methods using molecular oxygen as the stoichiometric reagent. These methods represent an interesting and highly atom-efficient alternative, as oxygen is cheap, readily available, and an oxidant that produces water as the only by-product. Aerobic oxidation is, however, strongly dependent on a good heterogeneous catalyst which facilitates efficient oxygen activation. The most common catalysts which have been applied for transformations involving aerobic oxidation are based on precious metals, like e.g. Au, Pt and Pd [2, 3]. These metals are expensive and scarce. Thus, in order to make such reactions industrially viable it is therefore important to develop new catalyst systems that comprise less expensive and more readily available, environmentally friendly components.

In this work, we present results from our initial screening of potential catalysts for the conversion of 5-hydroxymethyl furfural (HMF) to 2,5-furandicarboxylic acid (FDA), using molecular oxygen as oxidant. The catalysts contain 5 wt% metal, as metal oxides, on TiO_2 support, and the metals chosen are abundant, inexpensive first row transition metals, Figure 1.

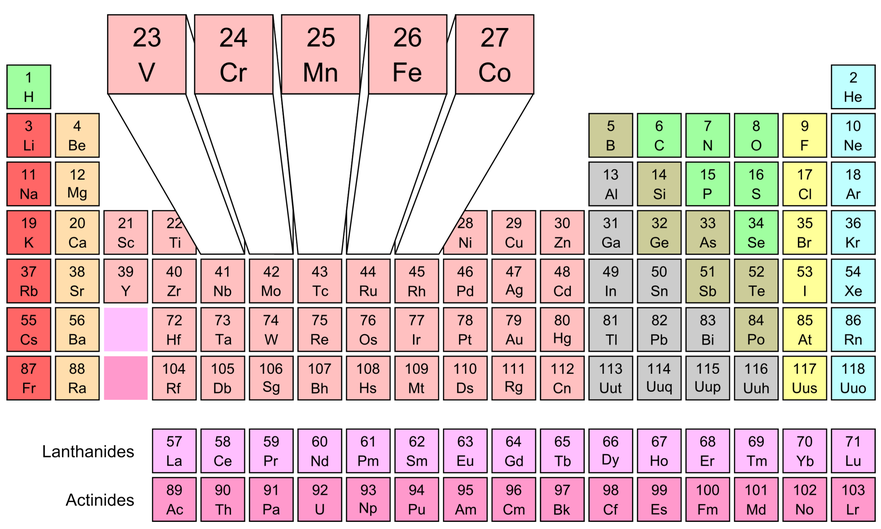

Figure 1: Metals tested for catalytic activity in HMF oxidation.

Why HMF?

- HMF can be obtained from biomass via dehydration of hexose monosaccharides, such as glucose or fructose [3].
- HMF is a precursor for many compounds with high industrial potentials, such as:
  - **2,5-furandicarboxylic acid (FDA)**
  - 5-hydroxymethylfuranoic acid (HMFCA)
  - 2,5-furandicarboxaldehyde (DFF)
- FDA has been identified as an important value added chemical by the U.S. Department of Energy biomass program [4].
- FDA can replace chemicals derived from fossil fuels in manufacture of polyamides, polyesters, and polyurethanes.

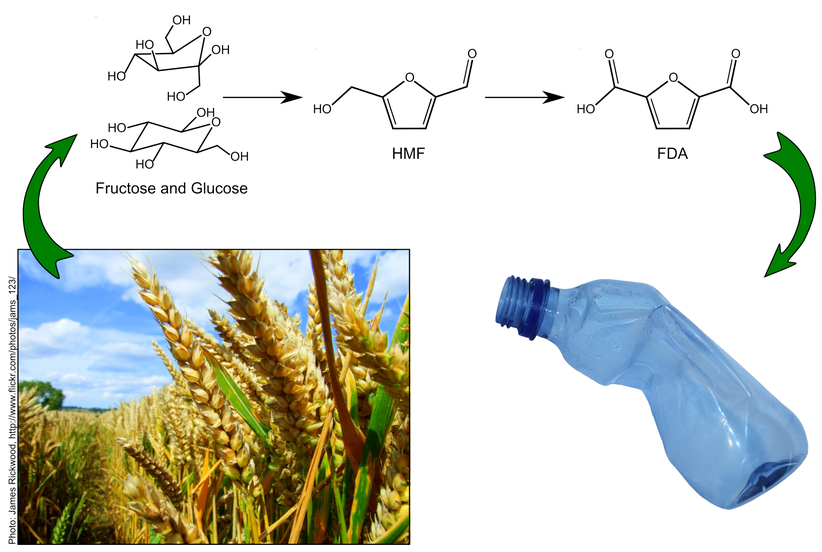

Figure 2: From biomass to polymer.

Experimental and Results

All catalysts were prepared using incipient wet impregnation, and calcinated after impregnation at suitable temperatures.

Reaction conditions for catalyst screening: 0.5 mmol HMF, 10 mL H_2O, P_{O_2}=10 bar, 4 hours + heating and cooling down. The samples were analyzed by HPLC.

Table 1: Airobic oxidation of HMF with 5 wt% metal/TiO_2 catalysts.

Metal	T [°C]	HMF Conv. [%]	Yield FDA [%]	Yield DFF [%]	Yield HMFCA [%]	Major product
V	140	100	< 1	4.2	< 1	Formic acid
	120	97	< 1	4.5	< 1	Formic acid
Cr	140	7	< 1	5.0	< 1	Formic acid
Mn	140	42	< 1	1.7	< 1	Formic acid
	120	33	< 1	2.3	< 1	Formic acid
	100	9	< 1	< 1	< 1	Formic acid
Fe	140	97	< 1	1.3	< 1	Formic acid
Co	140	47	< 1	< 1	< 1	Formic acid
	120	13	< 1	< 1	< 1	Formic acid
	100	0	–	–	–	–

Conclusions

As shown in Table 1 none of the tested compounds are suitable catalysts for oxidation of HMF. The selectivity towards FDA, the desired product, was in all cases extremely poor and milder conditions, such as lower reaction temperature, did not increase selectivity to FDA nor did it decrease yield of the undesired formic acid.

Formation of partially oxidized products, such as DFF or HMFCA was observed in most cases, but in very low yields. On the other hand, formation of unidentified degration products and polymers was observed when the conversion of HMF was high, which also indicates that the examined catalysts are not suitable for this kind of reactions.

Recent studies have, however, shown mixed oxides to be good catalysts for the oxidation of HMF, and under the appropriate conditions these oxides give excellent yields of FDA.

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Acknowledgements

This work was supported by the Danish National Advanced Technology Foundation and Novozymes A/S.